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## Thermogravimetric Kinetic Analysis of the Pyrolysis of Rice Straw

Nithitorn Kongkaew<sup>a\*,b</sup>, Witchaya Pruksakit<sup>b</sup>, Suthum Patumsawad<sup>a</sup>

<sup>a</sup>Department of Mechanical & Aerospace Engineering, Faculty of Engineering, King Mongkut's University of Technology North  
Bangkok (KMUTNB) 1518 Pracharat 1 Road, Wongsawang, Bangsue, Bangkok, Thailand 10800

<sup>b</sup>The Joint Graduate School of Energy and Environmental (JGSEE) 126 Prachauthit Road, Bangmod, Tungkru, Bangkok, Thailand  
10400

### Abstract

A kinetic of the pyrolysis of rice straw is investigated with thermogravimetric analyzer with non-isothermal methods selected for analyzing solid-state kinetics data is presented. The weight loss was measured by TGA in nitrogen atmosphere. The samples were heated over a range of temperature from 298 K to 973 K with three different heating rates of 5, 10 and 15 K min<sup>-1</sup>. The results obtained from thermal decomposition process indicate that there are two main stages such as active and passive pyrolysis. In the DTG thermograms the temperature peaks at maximum weight loss rate changed with increasing heating rate. The activation energy and pre-exponential factor obtained by Kissinger method are 172.62 kJ mol<sup>-1</sup>, 1.456 × 10<sup>11</sup> min<sup>-1</sup>, while, the same average parameters calculated from FWO and KAS methods are 192.66 kJ mol<sup>-1</sup>, 1.287 × 10<sup>22</sup> min<sup>-1</sup> and 193.60 kJ mol<sup>-1</sup>, 6.887 × 10<sup>15</sup> min<sup>-1</sup>, respectively. Experimental results showed that values of kinetic parameters obtained from three different methods are in good agreement, but KAS and FWO methods are more efficient in the description of the degradation mechanism of solid-state reactions.

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**Keywords:** rice straw; pyrolysis; thermogravimetric analysis; kinetics; isoconversional method

### 1. Introduction

An understanding of biomass pyrolysis can give rise to a development of biomass conversion process. Since pyrolysis is the first step of biomass conversion such as gasification, liquefaction, carbonization and

\* Corresponding author. Tel.: +66-81-832-4924; fax: +66-2-913-1926  
E-mail address: [k.nithitorn@gmail.com](mailto:k.nithitorn@gmail.com)

combustion, its sound understanding is significant for the effective use of biomass. For engineering applications, knowledge of the pyrolysis kinetics is essential for predicting the pyrolysis behaviour of biomass material as well as designing the suitable reactor design and operating condition which the correctness of the kinetic expression heavily depends upon reliable evaluation of kinetic parameters from the decomposition behaviour under different conditions of temperature and/or environment.

### Nomenclature

A	Pre-exponential factor ( $s^{-1}$ )
$\alpha$	conversion (-)
k	reaction rate constant ( $s^{-1}$ )
$m_a$	actual mass (kg)
$m_i$	initial mass (kg)
$m_f$	final mass (kg)
n	reaction order (-)
R	gas constant ( $J\ mol^{-1}\ K^{-1}$ )
$R^2$	correlation coefficient
T	Temperature (K)
$T_m$	Maximum temperature peak (K)
$\beta$	Heating rate ( $K\ min^{-1}$ )

The main purpose of this study was to approach the pyrolysis of rice straw by thermogravimetric analysis. Furthermore the present study provides a comparison of selected methods for analysing non-isothermal solid state kinetic data and investigate the kinetics of thermal decomposition to describe the pyrolysis process. The pyrolysis process was performed by TGA in nitrogen atmosphere and the thermal analysis curves were recorded at several linear heating rates. Three model-free (Kissinger, Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose) non-isothermal methods were used to calculate Arrhenius parameters and to verify which of them allow to detect reaction mechanisms of pyrolysis process. The effect of heating rate on decomposition was also studied.

## 2. Experimental and methodology

### 2.1. Experimental

Thermogravimetric Analysis, TGA was performed using Perkin Elmer, Pyris1 analyzer. To maintain pyrolysis conditions, high purity nitrogen was used as the carrier gas with  $50\ ml\ min^{-1}$  of volume flow rate. TGA for drying step had a heating rate of  $10\ K\ min^{-1}$  for all analysis, while pyrolysis step were performed at three different heating rates: 5, 10 and  $15\ K\ min^{-1}$ . Weight sample was 5 mg. The sample was put in a ceramic crucible each time and first dried from laboratory temperature to 378 K and the

heated from 378 to 973 K. During the heating, the mass of the rice straw and furnace temperature were record.

Table 1. Characteristic of rice straw

Proximate analysis (wt %)				Ultimate analysis (wt %)			
Moisture	Volatile	Fix carbon	Ash	C	H	N	O
9.79	65.78	13.97	10.46	45.56	7	0.77	46.67

## 2.2 Kinetic theory

Kinetic analysis techniques have been classified as either model-fitting (i.e., identification of kinetic reaction model) or isoconversional (i.e., model-free). Modern thermal analysis appears to prefer the use of the latter methods for two main reasons [1]: 1) model-free kinetics is sufficiently flexible to allow for a change of mechanism during the course reaction; 2) mass transfer limitations are reduced by the use of multiple heating rates. By contrast, model fitting kinetic methods generally involve a single heating rate, the disadvantage being that activation energy varies with heating rate due to mass/energy transfer effects. In this study intrinsic reaction rate coefficients are obtained for the pyrolysis of rice straw under differential heating conditions as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where  $t$  is time,  $k(T)$  the temperature-dependent constant and  $f(\alpha)$  a function called reaction model, which describes the dependence of the reaction rate on the extent of reaction,  $\alpha$ . The temperature dependence of the rate constant is described by the Arrhenius equation. Thus, the rate of solid-state reaction can be described by,

$$\frac{d\alpha}{dt} = A \exp(-E/RT) f(\alpha) \quad (2)$$

where  $A$  is the pre-exponential Arrhenius factor,  $E$  the activation energy and  $R$  the gas constant. For dynamic data obtained at a constant heating rate ( $\beta = dT/dt = \text{constant}$ ), this term is inserted in Eq. (2) so the above rate expression can be transformed into non-isothermal rate expression describing reaction as a function of temperature at a constant  $\beta$ .

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp(-E/RT) f(\alpha) \quad (3)$$

Integrating up to conversion,  $\alpha$ , Eq. (3) gives,

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp(-E/RT) dT \quad (4)$$

Isoconversional methods involve carrying out a series of experiments at different heating rates [2].

## 2.3 Model free methods

### • Kissinger method

Kissinger [3] developed a model-free non-isothermal method where is no need to calculate  $E_a$  for each conversion value in order to evaluate kinetic parameters. This method allows to obtain the value of activation energy from a plot of  $\ln(\beta/T_m^2)$  against  $1000/T_m$  for a series of experiments at different heating rates ( $\beta$ ), where  $T_m$  is the temperature peak of the DTG curve. The equation is the following:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (5)$$

The activation energy  $E_a$  can be calculated from the slope of the plot which is equal to  $-E_a/R$ .

- *Flynn-Wall-Ozawa (FWO) method*

The FWO method [4] allows to obtain apparent activation energy ( $E_a$ ) from a plot of natural logarithm of heating rates,  $\ln \beta_i$  versus  $1000/T_{ai}$  which represents the linear relation with a given value of conversion at different heating rates.

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E_\alpha}{RT_{ai}} \quad (6)$$

where  $g(\alpha)$  is constant at a given value of conversion. The subscript  $i$  and  $\alpha$  denotes given value of heating rate and given value of conversion, respectively. The activation energy  $E_a$  is calculated from the slope  $-1.052E_a/R$ .

- *Kissinger-Akahira-Sunose (KAS) method*

The KAS method [5] is based on the following expression:

$$\ln\left(\frac{\beta_i}{T_{ai}^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha g(\alpha)}\right) - \frac{E_\alpha}{RT_{ai}} \quad (7)$$

The apparent activation energy can be obtained from a plot of  $\ln(\beta_i/T_{ai}^2)$  versus  $1000/T_{ai}$  for a given value of conversion,  $\alpha$ , where the slope is equal  $-E_a/R$ .

### 3. Result and discussion

#### 3.1 Thermogravimetric analysis

Differential mass loss (DTG) thermograms of thermal decomposition of rice straw pyrolysis, at three heating rates 5, 10 and 15 K min<sup>-1</sup> under nitrogen atmosphere, are shown in Fig. 1. As it may be observed two regions are evident which correspond to active and passive pyrolysis. The main pyrolysis process proceeds in a range from approximately 450 K to 600 K. The weight loss curve (TG) in Fig. 1a shows the loss of mass with temperature at different heating rates of rice straw. As can be seen from the plot, the pyrolysis process begins at about 450 K proceeds rapidly with increasing temperature until about 600 K and then weight loss decrease slowly to the final temperature. The solid residue yields are about 30% for rice straw. The heating affects to TG curves positions, maximum decomposition rate and location of maximum  $T_m$  peaks. The Fig. 1a shows DTG curves of rice straw. When heating rate increases, starting and final temperature of active and passive pyrolysis period also increase. Maximum points of TG and minimum points of DTG curves are shifted towards higher temperature. This can be explained on the basis of heat transfer limitation. During the analysis, at low heating rate, a larger instantaneous thermal energy is provided to the system and a longer time may be required for the purge gas to reach equilibrium

with the temperature of the furnace of the sample. While at the same time and in the same temperature region a higher heating rate has a short reaction time and therefore the temperature needed for the sample to decompose is also higher. This causes the maximum rate curve to shift to the right [8, 9].

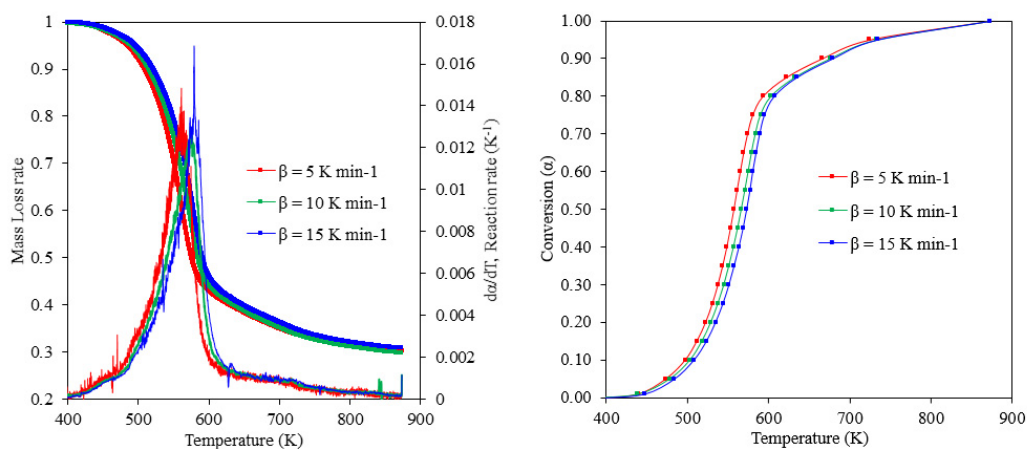


Fig. 1. (a) DTG; (b) TG of rice straw recorded in nitrogen at different heating rates.

### 3.2 Kinetic analysis

The results obtained from thermogravimetric analysis were elaborated according to model-free methods to calculate the kinetic parameters. The activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) were obtained using Kissinger, FWO and KAS methods. In the first method the  $E_a$  and  $A$  were calculated from Eq. (5), where  $T_m$  is temperature which corresponds to the maximum weight loss peaks. The peak temperatures were obtained from Fig. 1a. Kissinger plot of  $\ln(\beta/T_m^2)$  versus  $1000/T_m$  K<sup>-1</sup> of pyrolysis process for rice straw shown in Fig. 2. The regression equations and the square of the correlation coefficient ( $R^2$ ) is also presented. The activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) were derived from the slope and intercept of plotting regression line, respectively. The results obtained from Kissinger method are 172.62 kJ mol<sup>-1</sup> and  $1.46 \times 10^{11}$  min<sup>-1</sup> for activation energy and pre-exponential factor, respectively.

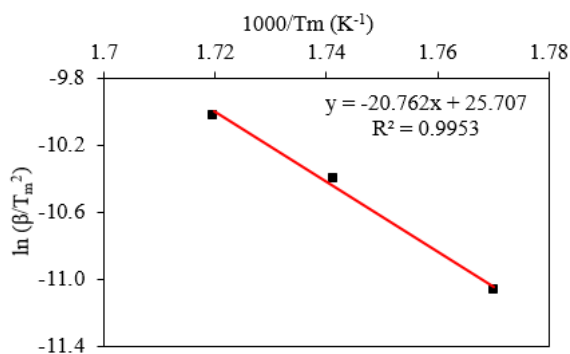


Fig. 2. Kissinger plot of rice straw.

The kinetic parameters obtained by FWO and KAS methods were calculated according to Eq. (6) and (7), respectively, for a given value of conversion,  $\alpha$ . Fig. 1b shows the change of the conversion with temperature of the rice straw samples at any moment at different heating rate. To determine the kinetic parameters, we chose the same value of  $\alpha$  from range 0.05 to 0.8 for all curves at different heating rate and we found the corresponding temperature. The FWO plot  $\ln \beta_i$  versus  $1000/T_{ai}$  K<sup>-1</sup> for different values of conversion are shown in Fig. 3a. The KAS plots of  $\ln(\beta_i/T_{ai}^2)$  versus  $1000/T_{ai}$  K<sup>-1</sup> for different values of conversion are shown in Fig. 3b. The apparent activation energies were obtained from the slope and pre-exponential factors from the intercept of regression lines and are given in Table 2. The calculated squares of the correlation coefficients,  $R^2$ , correspond to linear fittings in Figs. 3a and 3b, were higher for all cases and were from 0.975 to 0.996.

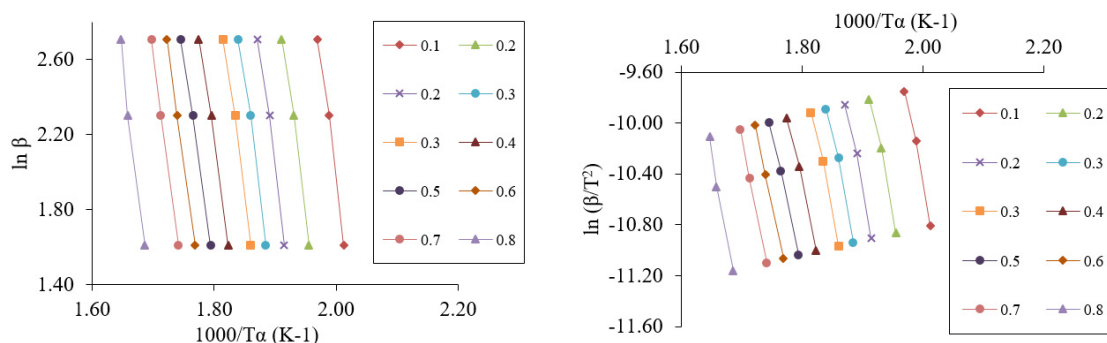


Fig. 3. (a) FWO; (b) KAS plot of rice straw for different values of conversion.

From Table 2, we can observe that apparent activation energy for FWO and KAS methods was not similar for all conversion indicates the existence of a complex multi-step mechanism that occurs in the solid state. The apparent value of activation energy is about 180.54–220.27 kJ mol<sup>-1</sup> and 181.95–221.72 kJ mol<sup>-1</sup> for FWO and KAS, respectively. This means that the reaction mechanism is not the same in the whole pyrolysis process and that activation energy dependent on conversion.

The model-free isoconversional methods allow to estimate activation energy as a function of conversion without previous assumption on the reaction model and allows nearly unmistakably detecting multi-step kinetics as a dependence of activation energy on conversion in contradistinction to Kissinger method which producing a single value of the  $E_a$  for the whole process and complexity may not be revealed [10]. The values of activation energy obtained from Kissinger method (172.62 kJ mol<sup>-1</sup>) are consistent with the range of values obtained by the FWO and KAS methods and very near to their average values, which are equal 192.66 and 193.60 kJ mol<sup>-1</sup>; the value of the pre-exponential factor is also contained in a region of average value.

Table 2. The results of  $E_a$  and  $A$  for a rice straw obtained by FWO, KAS and Kissinger methods,  $R^2$  corresponding to linear fittings in Figs 3a and 3b.

Conversion, $\alpha$	FWO method			KAS method		
	$E_a$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$R^2$	$E_a$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$R^2$
0.05	180.54	$4.32 \times 10^{21}$	0.9599	181.95	$2.56 \times 10^{15}$	0.9564
0.10	203.61	$1.40 \times 10^{23}$	0.9924	205.82	$7.54 \times 10^{16}$	0.9917
0.15	195.28	$4.21 \times 10^{21}$	0.9899	196.81	$2.13 \times 10^{15}$	0.9890
0.20	199.08	$3.87 \times 10^{21}$	0.9886	200.62	$1.88 \times 10^{15}$	0.9876
0.25	193.42	$4.71 \times 10^{20}$	0.9887	194.52	$2.21 \times 10^{14}$	0.9876
0.30	190.40	$1.28 \times 10^{20}$	0.9921	191.21	$5.85 \times 10^{13}$	0.9913
0.35	187.99	$4.51 \times 10^{19}$	0.9931	188.59	$2.01 \times 10^{13}$	0.9924
0.40	181.47	$6.67 \times 10^{18}$	0.9945	181.64	$2.93 \times 10^{12}$	0.9939
0.50	177.24	$1.32 \times 10^{18}$	0.9979	177.03	$5.60 \times 10^{11}$	0.9976
0.60	186.14	$5.41 \times 10^{18}$	0.9997	186.27	$2.24 \times 10^{12}$	0.9997
0.70	196.53	$2.77 \times 10^{19}$	0.9993	197.05	$1.11 \times 10^{13}$	0.9993
0.80	220.27	$1.08 \times 10^{21}$	0.9907	221.72	$4.07 \times 10^{14}$	0.9899
<b>Average</b>	<b>192.66</b>	<b><math>1.29 \times 10^{22}</math></b>		<b>193.60</b>	<b><math>6.89 \times 10^{15}</math></b>	
<b>Kissinger</b>		<b>172.62</b>			<b><math>1.456 \times 10^{11}</math></b>	

#### 4. Conclusion

In this study, an experimental kinetic study of rice straw pyrolysis is presented where kinetic constants were determined and compared through three different methods. Thermogravimetric analysis was investigated under nitrogen atmosphere at different heating rates of 5, 10 and 15 K min<sup>-1</sup>. Pyrolysis of rice straw proceeds in two steps as active and passive pyrolysis. It was found that the mainly pyrolysis process occurred about 450–740 K. Effect of heating rate on TG and DTG curves was also presented. Activation energy and pre-exponential factor were obtained by the model-free methods. The kinetic parameters calculated by Kissinger method were the same for the whole pyrolysis process, whereas in the FWO and KAS methods apparent activation energy and apparent pre-exponential factor vary with conversion and revealed the complex mechanism of reaction that occur during the pyrolysis process.

The values of activation energy obtained from the Kissinger method (172.62 kJ mol<sup>-1</sup>) are consistent with the range of values obtained by the FWO and KAS methods and is very near to their average values which are equal 192.66 and 193.60 kJ mol<sup>-1</sup>; the value of the pre-exponential factor also contained in a period of average value. Experimental results showed that values of kinetic parameters are good agreement and that the model-free methods, mainly FWO and KAS, satisfactory described the complexity of pyrolysis process.

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